

**Sampling and Analysis Plan for Enhanced In Situ
Bioremediation Predesign Operations Test Area
North, Operable Unit 1-07B**

Published February 2001

**Idaho National Engineering and Environmental Laboratory
Environmental Restoration Directorate
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Restoration
Bechtel BWXT Idaho, LLC
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727**

ABSTRACT

This Sampling and Analysis Plan describes the sampling support of the enhanced in situ bioremediation predesign operations, which are being performed to monitor reductive dechlorination of trichloroethene and to determine whether secondary source mobilization is occurring as a result of electron donor addition.

The sampling activities described in this plan include two components. The first is performance monitoring during the predesign operations period. This activity will entail routine groundwater sampling to ensure that continual trichloroethene dechlorination is occurring through electron donor addition and to monitor the efficiency of the process. The second component is monitoring to determine whether electron donor injection results in the mobilization of metals, Sr-90, and/or Cs-137.

CONTENTS

ABSTRACT	iii
ACRONYMS.....	ix
1. INTRODUCTION.....	1-1
1.1 Sampling Approach	1-1
1.2 Site Background.....	1-1
2. OBJECTIVES	2-1
2.1 Problem Statement.....	2-1
2.1.1 Performance Monitoring.....	2-1
2.1.2 Secondary Source Mobilization Sampling	2-1
2.2 Decision Identification.....	2-2
2.2.1 Performance Monitoring.....	2-2
2.2.2 Secondary Source Mobilization Sampling	2-2
2.3 Decision Inputs	2-2
2.3.1 Performance Monitoring.....	2-2
2.3.2 Secondary Source Mobilization Sampling	2-2
2.4 Study Boundaries.....	2-4
2.4.1 Performance Monitoring.....	2-4
2.4.2 Secondary Source Mobilization Sampling	2-4
2.5 Decision Rule.....	2-4
2.5.1 Performance Monitoring.....	2-4
2.5.2 Secondary Source Mobilization Sampling	2-5
2.6 Decision Error Limits	2-5
2.7 Design Optimization.....	2-5
3. SAMPLE LOCATION AND FREQUENCY	3-1
3.1 Sampling Location.....	3-1
3.2 Sampling Frequency and Analytes	3-1
3.3 Presampling Meeting	3-2

3.4	Sample Designation	3-2
4.	SAMPLING EQUIPMENT AND PROCEDURES	4-1
4.1	Groundwater Elevations	4-1
4.2	Well Purging	4-1
4.3	Groundwater Sampling	4-1
4.4	Field Analyses	4-2
4.5	Radiological Screening and Shipping	4-2
5.	SAMPLE HANDLING AND ANALYSIS	5-1
5.1	Sample Handling	5-1
5.1.1	Sample Preservation and Preparation	5-1
5.1.2	Chain-of-Custody	5-1
5.1.3	Transportation of Samples	5-1
5.2	Sample Analysis	5-1
5.2.1	Chloroethenes	5-1
5.2.2	Ethene/Ethane/Methane	5-3
5.2.3	Electron Donor/Lactate	5-3
5.2.4	Acetate/Propionate/Butyrate	5-3
5.2.5	Tritium	5-3
5.2.6	Beta-and Gamma Emitters	5-3
5.2.7	Alpha Emitters	5-3
5.2.8	Metals	5-3
5.2.9	Field Analyses	5-3
6.	WASTE MANAGEMENT	6-1
7.	QUALITY ASSURANCE	7-1
7.1	Laboratory Performance Evaluation	7-2
8.	REFERENCES	8-1

FIGURES

1-1. Site map and monitoring locations.....	1-2
---	-----

TABLES

2-1. Predesign operations period task responsibilities.....	2-1
2-2. Decision inputs for ISB performance monitoring.	2-3
2-3. Decision inputs for secondary source mobilization sampling.....	2-4
3-1. Performance monitoring.....	3-1
3-2. Secondary source mobilization sampling.....	3-2
4-1. Well purge water volumes.....	4-1
5-1. Specific requirements for groundwater samples to be analyzed onsite.....	5-2
5-2. Offsite analyses.	5-2
5-3. Field analyses.	5-2
7-1. Quality assurance/quality control samples for groundwater analyses.....	7-1
7-2. Specific requirements for groundwater split samples.	7-2
7-3. Summary of performance evaluation program for water samples.	7-3
7-4. Acceptance criteria for analytical accuracy in water performance evaluation analyses.	7-4

ACRONYMS

ALS	Alpha Spectometry
ASTU	Air Stripper Treatment Unit
CFR	Code of Federal Regulations
COC	chain of custody
DO	dissolved oxygen
DQO	data quality objective
ECD	Electron Capture Detector
EPA	Environmental Protection Agency
ER	Environmental Restoration
FEWP	Field Evaluation Work Plan
FID	Flame Ionization Detector
GC	Gas Chromatography
GFP	Gas Flow Proportional
HDPE	high-density polyethylene
IC	Ion Chromatography
ID	identification
INEEL	Idaho National Engineering and Environmental Laboratory
IRC	INEEL Research Center
ISB	in situ bioremediation
LSC	liquid scintillation counting
MCP	Management Control Procedure
ORP	Oxidation Reduction Potential
PE	performance evaluation
QAPjP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan

SMO	Sample Management Office
SOW	Scope of Work
TAN	Test Area North
TCE	trichloroethene
TPR	technical procedure
TSF	Technical Support Facility
VOC	volatile organic compound

Sampling and Analysis Plan for Enhanced In Situ Bioremediation Predesign Operations Test Area North, Operable Unit 1-07B

1. INTRODUCTION

In situ bioremediation (ISB) predesign operations are scheduled to begin in October 2000 and continue through September 2004. This phase consists of continued ISB system operations, including groundwater monitoring. The most cost-effective operations strategy will be determined during ISB predesign operations. Scope of these activities is described in the *Field Demonstration Report, Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2000).

The field sampling plan provides the details for monitoring during the ISB predesign operations period. Formally, the sampling and analysis plan for this activity is comprised of this sampling plan together with the *Quality Assurance Project Plan for Waste Area Groups 1, 2, 3, 4, 5, 6, 7, 10, and Inactive Sites* or QAPjP (DOE-ID 1997). These plans have been prepared pursuant to the *National Oil and Hazardous Substances Contingency Plan* (EPA 1990) and sampling and analysis plan preparation guidelines from the United States Environmental Protection Agency (EPA). The field sampling plan describes the field activities and the analyses to be performed, while the QAPjP details the processes and programs that ensure generated data are suitable for their intended use. This plan is organized in accordance with Management Control Procedure (MCP)-241, "Preparation of Characterization Plans."

1.1 Sampling Approach

The sampling described in this plan is being performed to support the objectives of predesign operations, which are to ensure continual trichloroethene (TCE) dechlorination and to determine whether secondary source mobilization is occurring as a result of electron donor addition. The area to be evaluated is shown in Figure 1-1. Electron donor will continue to be injected during the predesign operations period. It is estimated that electron donor will be injected on a six to eight week interval. The electron donor injection strategy may be modified as needed to support the objectives outlined for the predesign operations period. All of the monitoring locations to be sampled are shown on Figure 1-1 and the exact locations, frequencies, and analytes are presented in Section 3.

The sampling activities described in this plan include two components. The first is performance monitoring during the predesign operations period. This activity will entail routine groundwater sampling to ensure that continual TCE dechlorination is occurring through electron donor addition and to monitor the efficiency of the process. The second component is monitoring to determine whether electron donor injection results in the mobilization of metals, Sr-90, and/or Cs-137. These two components of the sampling activities are addressed separately throughout this plan for clarity.

1.2 Site Background

The Technical Support Facility (TSF)-05 injection well was used over a 15 to 20-year period to dispose of all liquid waste streams generated by operations at Test Area North (TAN). These waste streams included low-level radioactive wastewater, industrial wastewater including dissolved and possibly pure phase organic liquids, and sanitary sewage. The result of this waste injection into the Snake River Plain Aquifer has resulted in a nearly 3-km (2-mi) long plume of contamination. Detailed descriptions of the historical background can be found in the Remedial Investigation report

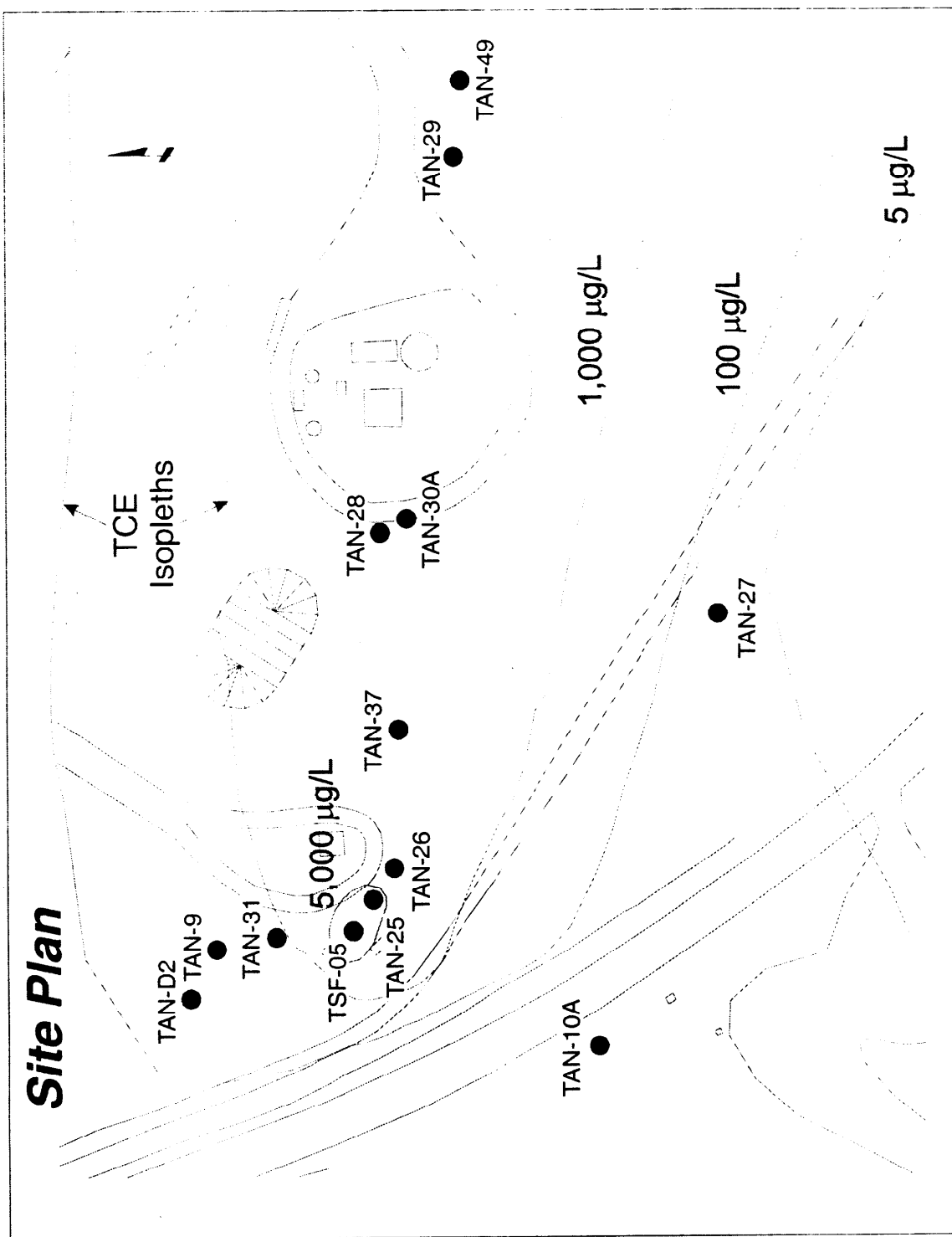


Figure 1-1. Site map and monitoring locations.

(Kaminski et al. 1994) and in the record of decision (DOE-ID 1995). The contaminants of concern in groundwater at the site include the volatile organic compounds (VOCs) TCE, tetrachloroethene, trans-1,2-dichloroethene, and cis-1,2-dichloroethene as well as the radionuclides tritium, Sr-90, Cs-137, and potentially uranium-234. The hazards associated with sampling, given the concentrations of these contaminants in groundwater, have been well characterized and are addressed in the health and safety plan (INEEL 1998).

2. OBJECTIVES

The sampling objectives are discussed in the context of the data quality objectives (DQOs) process as defined by *Data Quality Objectives Process for Superfund, Interim Final Guidance* (EPA 1994). This process was developed by the EPA to ensure that the type, quantity, and quality of data used in decision making are appropriate for the intended application. The process includes several steps, each of which has specific outputs that together form the DQOs for a given project. The DQO process has been used for this sampling activity in accordance with MCP-227, "Sampling and Analysis Process for Environmental Management Funded Activities." Each of the following subsections corresponds to a step in the DQO process and the output for each step is provided as appropriate.

2.1 Problem Statement

The first step in the DQO process is simply to state the problem to be addressed and to put it in its programmatic context. The appropriate problem statements as they apply to each of the major sampling activities are given in the sections below. Another output of this step, common to all of the activities, is an estimate of the budget, schedule, and personnel. The budget and schedule are addressed in the ISB predesign work plan. The personnel responsible for the sampling activities are presented in Table 2-1.

2.1.1 Performance Monitoring

It is desired to achieve maximum contaminant degradation at the lowest possible cost. This will require that system performance be carefully monitored for different operating strategies.

2.1.2 Secondary Source Mobilization Sampling

It is necessary to determine if the remediation process is mobilizing compounds, which may adversely affect the downgradient aquifer. Samples will be collected for metals, Sr-90 and Cs-137 analysis.

Table 2-1. Predesign operations period task responsibilities.

Functional Role	Responsible Organization	Person
Operable Unit 1-07B project manager	INEEL	J.S. Rothermel
ISB technical lead	INEEL	K.S. Sorenson
Sampling and analysis field team leader	INEEL	D. Shanklin
ISB Predesign project engineer	INEEL	L.O. Nelson
Engineering and operations		
– Operations Strategy	INEEL	K.S. Sorenson
– Design	INEEL	A.J. Cram
– Field Operations Supervisor	INEEL	M.E. Bartholomei
– Groundwater monitoring field coordinator	INEEL	M.E. Feldman

2.2 Decision Identification

This step in the DQO process is used to identify the decisions and the potential actions that will be affected by the data collected. These outputs are discussed below with respect to each of the sampling activities.

2.2.1 Performance Monitoring

The most appropriate electron donor addition strategy will be determined by the data collected through performance monitoring. The possible actions are to continue with the current injection strategy or to change the strategy based on field observations.

2.2.2 Secondary Source Mobilization Sampling

The objective of this sampling is to determine whether metals, Sr-90 and/or Cs-137 are being mobilized from the source area and have been determined to be a detriment to the downgradient aquifer due to electron donor addition.

2.3 Decision Inputs

Decision inputs are the parameters required to help make the decision identified in the previous section. For predesign operations the decision inputs are comprised primarily of performance monitoring analytes.

2.3.1 Performance Monitoring

Performance monitoring throughout the predesign operations period is being performed to determine the most appropriate electron donor addition strategy. This requires an understanding of system efficiency under different strategies. The results of the field evaluation and Predesign Phase I showed that system efficiency is a function of electron donor distribution, electron donor type(s), and redox conditions. The suite of analytes serving as inputs for the strategy have been selected based on these results. The inputs are summarized in Table 2-2. The analyte list is an abbreviated list of those identified in the *Enhanced In Situ Bioremediation Field Evaluation Work Plan* (ISB FEWP, DOE-ID 1998). A discussion of the abbreviated analyte list can be found in Section 2.7.

2.3.2 Secondary Source Mobilization Sampling

The enhanced biological activity in the residual source area has dramatically affected the redox conditions and the geochemistry. Given these effects, some potential exists that contaminants previously sequestered in the area will be released to the aqueous phase. In the case of organic contaminants, this may be desirable because it increases their bioavailability, facilitating in situ biodegradation. Sampling for SVOCs was performed during PDP-IIb to evaluate this possibility. Of particular interest are the inorganic contaminants, radionuclides and metals, which are not biodegraded. The analytes serving as inputs for this determination are shown in Table 2-3.

Table 2-2. Decision inputs for ISB performance monitoring.

Parameter	Significance	Potential Analytical Method	Prec./Acc.
Chlorinated Ethenes	Contaminants and dechlorination products; required to determine effectiveness of enhanced ISB.	Gas Chromatography (GC)/ Electron Capture Detector (ECD)	±25%
Ethene/Ethane/ Methane	Dechlorination products and redox indicator; required to determine effectiveness of enhanced ISB.	GC/Flame Ionization Detector (FID)	±25%
Electron Donor (Lactate)	Added electron donor; required to determine extent of biostimulation.	Ion Chromatography (IC)	±25%
Acetate/Propionate/ Butyrate	Anaerobic by-product; required to assess the anaerobic activity.	GC/FID	±50%
Sulfate	Electron acceptor; required to assess active anaerobic reaction pathways.	Hach Field Test Kit	±50%
Chemical Oxygen Demand	Indirect measure of biomass and redox conditions; useful for evaluating biostimulation (electron donor distribution).	Hach Field Test Kit	±50%
Tritium	Conservative compound used to account for geochemistry changes not due to enhanced ISB.	Radiochemistry—Tritium in water (Revision 4) Liquid scintillation counting	±25%
Temperature/pH/ Conductivity/ Dissolved Oxygen (DO)/Oxidation Reduction Potential (ORP)	Water quality parameters; may be useful for evaluating biostimulation and suitability of conditions for anaerobic reductive dechlorination.	Flow-through cell during groundwater sampling	±10%
Iron	Electron acceptor (Fe-III)/reduced product (Fe-II); required to assess active anaerobic reaction pathways.	Hach Field Test Kit	±50%
Alkalinity	Indicator of microbial respiration; may be useful for evaluating biostimulation.	Hach Field Test Kit	±25%

Table 2-3. Decision inputs for secondary source mobilization sampling.

Parameter	Significance	Potential Analytical Method	Prec./Acc.
Sr-90/ Cs-137/alpha emitters	To evaluate the possibility of contaminant mobilization during enhanced ISB.	Gas flow proportional Gamma spectrometry	
Metals	To evaluate the possibility of contaminant mobilization during enhanced ISB.	SW-846 6010B and 7000 series	

2.4 Study Boundaries

This step in the DQO process defines the boundaries of the study to clarify the sample domain. The boundaries include spatial boundaries and temporal boundaries. The spatial boundaries simply define the physical extent of the study area, and may be subdivided into specific areas of interest. The temporal boundaries define the duration of the study, or specific parts of the study. The appropriate outputs for each sampling activity are discussed in the following three sections.

2.4.1 Performance Monitoring

The spatial boundaries for both objectives of the performance monitoring and the secondary source mobilization sampling are the same. The boundaries of the treatment zone, as defined by the wells in Figure 1-1, are the study area boundaries. The temporal boundaries are defined by the duration of the predesign operations period, October 2000 through September 2004.

2.4.2 Secondary Source Mobilization Sampling

The spatial boundaries are the same as described for the performance monitoring in the previous section. The sample population will be represented by the axis of the treatment zone, where if mobilization of the secondary source were to occur it would be detected. The temporal boundaries are also defined by the duration of the predesign operations period. Samples will be collected throughout the predesign operations period on a quarterly basis for Cs-137, Sr-90, and metals.

2.5 Decision Rule

The objective of this step is to develop a logical statement that defines the conditions that would cause the decision maker to choose among alternative actions.

2.5.1 Performance Monitoring

It is desired to achieve maximum contaminant degradation at the lowest possible cost. This will require that system performance be carefully monitored for different operating strategies. If the dechlorination of TCE during a given strategy will not meet remedial action objectives then the operation strategy will be modified.

2.5.2 Secondary Source Mobilization Sampling

If field data show electron donor addition creates anomalous conditions the Agencies will be notified and appropriate response actions will be defined, discussed with the Agencies to reach concurrence, and implemented to insure that remedial action objectives will be met by 2095.

2.6 Decision Error Limits

The purpose of decision error limits is to establish appropriate performance goals for data uncertainty. However, the decisions to be made at the end of these activities are not amenable to quantitative decision errors, unlike decisions regarding the number of samples to collect when looking for contamination. Nevertheless, defining the allowable uncertainty in decision inputs is useful. These values are provided in Tables 2-2 and 2-3. For the analytes in Table 2-3, these values correspond to standard EPA specifications as noted in the QAPjP. For those in Table 2-2, the uncertainty allowable was based on a consideration of the importance of each individual data point for that analyte.

2.7 Design Optimization

The purpose of design optimization in the DQO process is to identify the best sampling and analysis design that satisfies all of the previous steps in the process. This includes identifying the data that need to be collected (analytes), their purpose, the appropriate analytical methods, and sampling locations and frequencies. The analytes, their purpose, and the analytical methods listed in Tables 2-2 and 2-3 will be used for these sampling activities. The sampling locations and frequencies are presented for both sampling activities in Section 3.

The field evaluation results have provided information that allows a reduced analyte list for performance monitoring. Based on the field evaluation results, TCE dechlorination was found to be strongly dependent on sulfate reduction and methanogenesis, therefore, sulfate and methane will continue to be sampled and analyzed. However, iron samples will also be collected and analyzed. The importance of the iron analysis is to monitor the amount of dissolved iron that may precipitate with sulfide or other dissolved ions. The analysis of both carbon dioxide and alkalinity samples provided redundant information. Alkalinity samples will be collected and analyzed instead of carbon dioxide samples based on the better precision with the alkalinity analysis. Chloride samples will no longer be collected and analyzed. The chloride analysis did not provide useful information due to the high background concentrations of chloride and the small concentration changes relative to the precision of the analytical method. The sampling frequency will also be lower due to less frequent lactate injections and a better understanding of how the system behaves. Sampling locations for total metals will be reduced to TAN-25, -26, -28, -29 and -31, based on results to date. It should be noted that the sampling frequency and analytes for given locations during performance monitoring are preliminary and may be changed based upon on-going analysis of data collected during predesign operations.

3. SAMPLE LOCATION AND FREQUENCY

The material presented in this section provides the practical details of the sampling and analysis strategy selected in Section 2. Field guidance forms outlining sample collection location, sample numbers, and analyses requested will be provided for each sample location by the Sample Management Office (SMO). The forms will be generated from the Integrated Environmental Data Management System database, which will ensure unique sample numbers. Sample and analysis tables for the groundwater analyses are provided as an attachment in this document.

3.1 Sampling Location

Samples will be collected from the wells outlined in Table 3-1. Refer to Figure 1-1 for an overview of all groundwater monitoring well locations. Wells TAN-37 and TSF-05 will each be sampled at two different depths, TAN-37A (shallow depth), TAN-37B (deeper depth), TSF-05A, and TSF-05B.

3.2 Sampling Frequency and Analytes

Performance monitoring will be conducted throughout the predesign operations period. The wells, sampling frequencies, and analytes are provided in Table 3-1. Samples will be collected to evaluate whether mobilization of the secondary source is occurring. The monitoring locations, frequencies, and analytes are presented in Table 3-2.

Occasionally, samples are collected for separately funded research projects to capitalize on the unique opportunity presented by the full-scale ISB system in deep, fractured rock at TAN. Sampling and analysis tables for research samples will be prepared as needed. In general, the collection of research samples will not involve a separate mobilization, but will take place during routine sampling in support of the predesign operations. The frequency of sampling and specific analytes required to support research activities vary depending on the needs of the researcher.

Table 3-1. Performance monitoring.

Well	Frequency	Analytes
TSF-05A	Monthly	Chloroethenes, Ethene/Ethane/Methane, Electron
TSF-05B	Monthly	Electron donor, Acetate/Propionate/Butyrate, Iron, Sulfate,
TAN-25	Monthly	Alkalinity, chemical oxygen demand, Temperature/pH/ORP/
TAN-26	Monthly	Conductivity/Dissolved Oxygen, and Tritium
TAN-31	Monthly	
TAN-37A	Monthly	
TAN-37B	Monthly	
TAN-28	Monthly	
TAN-30A	Monthly	
TAN-29	Monthly	
TAN-D2	Monthly	
TAN-10A	Monthly	
TAN-27	Monthly	

Table 3-2. Secondary source mobilization sampling.

Well	Frequency and Analytes
TSF-05A	<ul style="list-style-type: none">Quarterly for gamma emitters (Cs-137), Sr-90
TSF-05B	<ul style="list-style-type: none">Quarterly for total metals, at TAN-25, -26, -28, -29 and -31 only.
TAN-25	<ul style="list-style-type: none">Annually for alpha emitters
TAN-26	
TAN-31	
TAN-37A	
TAN-37B	
TAN-28	
TAN-30A	
TAN-29	
TAN-D2	
TAN-10A	
TAN-27	

3.3 Presampling Meeting

A plan of the day meeting will be conducted every day prior to the commencement of all sampling activities. The plan of the day meeting will focus on the sampling objectives, task-specific health and safety issues, and waste management. At this time the determination will be made whether a formal prejob briefing needs to be conducted.

3.4 Sample Designation

A systematic character sample identification (ID) code will be used to identify all samples uniquely, ensuring no two samples are assigned the same ID code. The first designator of the code, refers to Waste Area Group 1. The second and third designators will be "DO" (design operations) for samples collected in support of the predesign operations period. The next three numbers designate the sequential sample number for the project. A two character set (i.e., 01 = regular sample, 02 = duplicate) will be used next to designate replicate samples. The last two characters refer to a particular analysis. Refer to Section 4 for specific sample requirements.

For example, a groundwater sample collected from TAN might be designated as 1DO00101R8 where (from left to right):

- 1 designates the Waste Area Group
- DO designates that it is a sample collected in support of predesign operations
- 001 designates the sequential sample number

- 01 designates types of sample (i.e., regular sample)
- R8 designates tritium analysis by liquid scintillation counting (LSC).

A sampling and analysis plan (SAP) table will be used to record all pertinent information (monitoring location [well] designation, media, date, etc.) associated with each sample ID code. In an effort to minimize SAP discrepancies, SAP tables will be prepared prior to each sampling event. Any deviations from these SAP tables, which include samples not collected and/or additional samples collected, will be documented and included through the Document Action Request process.

4. SAMPLING EQUIPMENT AND PROCEDURES

This section addresses the sampling equipment and procedures to be used for the predesign operations period. The following major field components required to support the predesign operations period are discussed below: 1) groundwater elevation measurements, 2) well purging, 3) groundwater sampling, 4) field analyses, and 5) shipping.

4.1 Groundwater Elevations

Groundwater elevation measurements will be collected for a total of approximately three weeks prior to and after operations of the Air Stripper Treatment Unit (ASTU) located at well TAN-29 are suspended. These will be measured using pressure transducers connected to data loggers per the manufacturer's specifications. This will allow the hydraulic gradient before and after the ASTU is shut down to be measured.

4.2 Well Purging

All wells will be purged prior to sample collection using the micropurge method, according to "Ground Water Sampling Using the Micropurge Method," TPR-151 and "ISB Field Sampling Procedure," TPR-165. This applies to all groundwater sampling activities. The micropurge method was chosen due to waste management constraints and the need to have all wells sampled within the same day, if possible. The needed equipment and purging procedure are provided in the TPRs. Dedicated pumps will be used in all wells. The target pumping rate will be 4 to 6 L/min (1 to 1 ½ gpm). The estimated amount of purge water generated from each well for each sampling event is provided in Table 4-1.

Table 4-1. Well purge water volumes.

Well	Casing Diameter (in.)	Length of Casing ^a (ft)	Estimated Purge Volume ^b (gal)
TSF-05A	0.5	275	20
TSF-05B	0.5	275	20
TAN-25	1	218	27
TAN-26	1	389	48
TAN-31	1	258	32
TAN-37A	0.5	275	20
TAN-37B	1	379	47
TAN-28	1	240	30
TAN-30A	1	310	38
TAN-29	5	265	306*
TAN-D2	1	241	30
TAN-10A	1	233	29
TAN-27	1	235	29

a. Length of casing is measured from the middle of the screened interval to ground surface.

b. Purge volume is calculated per INEEL TPR-151. Volumes are based on a maximum of three well stand-pipe volumes.

* Purge volume calculated per INEEL TPR-157, "Groundwater Sampling," for a maximum five well volumes.

4.3 Groundwater Sampling

Groundwater samples will be collected for the analyses listed in Section 3.2 during the predesign operations period. All wells will be sampled per "ISB Field Sampling Procedure," TPR-165.

4.4 Field Analyses

Samples that will be analyzed in the field are described in Section 5. These analyses will be performed per TPR-166, "ISB Field Analyses Procedure."

4.5 Radiological Screening and Shipping

Samples collected from wells TAN-25, TAN-26, TAN-31, and TSF-05 will be surveyed for external radiological contamination prior to analysis or shipment. All other wells to be sampled have been historically free of radioactivity.

5. SAMPLE HANDLING AND ANALYSIS

5.1 Sample Handling

5.1.1 Sample Preservation and Preparation

Cooling of samples requiring 4°C preservation will be performed immediately upon sample collection (see Tables 5-1, 5-2, and 5-3). The temperature will be checked periodically prior to shipment to ensure adequate preservation. Coolers containing frozen reusable ice will be used to chill samples, as required. Sample bottles will be preserved prior to sample collection for those samples requiring chemical preservation. The pH will be checked after sample collection to ensure it is adequate for those samples requiring preservation at a pH≤2, except for those samples requiring a zero headspace (ethene/ethane/methane). Those samples that are shown in Table 5-2 will be analyzed offsite and will be handled and preserved per the governing task order statement.

Analyses that will be performed in the field are shown in Table 5-3. The priority indicated in Table 5-3 is a reflection of the holding times for those particular analyses. All of the field analyses will be performed per "ISB Field Analyses Procedure," TPR-166, and within 48 hours of sampling. Those with a priority of 1 or 2 will be analyzed as soon as possible after collection.

5.1.2 Chain-of-Custody

To maintain and document possession of samples shipped to a laboratory for analysis, chain-of-custody (COC) procedures will be followed per MCP-244 "Chain-of-Custody, Sample Handling and Packaging" and the QAPjP. The purpose of the COC is to document the identity of the sample and its handling from the point of collection until laboratory analysis is complete. The COC record is a multiple copy form, which serves as a written record of the sample handling. When a sample changes custody, the person(s) relinquishing and receiving the sample will sign a COC record. Each change of possession will be documented. The COC procedures will begin immediately after sample collection. The sample identification number, date, and time will be entered on the COC form the day of sample collection. Sample bottles will be stored in a secured area accessible only to the field team members. A COC will not be initiated for those samples that are analyzed onsite in the field laboratory. These samples will never leave the custody of the field team members.

5.1.3 Transportation of Samples

Samples will be transported in accordance with the regulations issued by the Department of Transportation (49 Code of Federal Regulations [CFR] Parts 171 through 178) and EPA sample handling, packaging, and shipping methods (40 CFR 261.C.3C.3). All samples will be packaged in accordance with the requirements set forth in INEEL MCP-244 "Chain-of-Custody, Sample Handling and Packaging" and the governing task order statement.

5.2 Sample Analysis

5.2.1 Chloroethenes

Chloroethenes will be measured using solid phase microextraction of aqueous samples, followed by injection into a gas chromatograph (GC) equipped with a flame ionization detector (FID). See the ISB FEWP SAP (Sorenson and Bullock 1999) for a more detailed description of the analysis. Analysis will

Table 5-1. Specific requirements for groundwater samples to be analyzed onsite.

Analytical Parameter	Size	Type	Preservative	Method	Holding Time
Chloroethenes	40-mL	Two Glass Vials	4°C	SW-846 8260 with GC/ECD	7 days
Ethene/Ethane/Methane	40-mL	Two Glass Vials	4°C and pH<2 with H ₂ SO ₄	SW-846 8015M with GC/FID	14 days
Electron Donor/Lactate	20-mL	One Glass Vial	4°C	IC	48 hours
Acetate/Propionate/Butyrate	20-mL	One Glass Vial	4°C	GC/FID	48 hours

Table 5-2. Offsite analyses.

Analytical Parameter	Size	Type	Preservative	Method	Holding Time
Tritium	125-mL	HDPE	None	LSC	6 months
Beta and Gamma Emitters	1-L	HDPE	pH<2 w/HNO ₃	GFP	6 months
Alpha Emitters	2-L	HDPE	pH<2 w/HNO ₃	ALS	6 months
Metals	1-L	HDPE	pH<2 w/HNO ₃	SW-846 methods	28 days

LSC = Liquid Scintillation Counting
HDPE = high-density polyethylene

GFP = Gas Flow Proportional

ALS = Alpha Spectrometry

Table 5-3. Field analyses.

Analytical Parameter	Preservation	Priority	Method	Precision
Temperature/pH/ORP/DO/Conductivity	NA	1	Hydrolab Measurements	0.5%/3%/2%/2%/1%
Iron	Cool, 4°C	2	Colorimetric	1%
Alkalinity	Cool, 4°C	3	Titrimetric	1%
Sulfate	Cool, 4°C	4	Colorimetric	1%
Chemical Oxygen Demand	Cool, 4°C and ratio of sample to H ₂ SO ₄ must remain 9:1	5	Colorimetric	20%

be performed at the Idaho National Engineering and Environmental Laboratory (INEEL) Research Center (IRC). Chloroethene samples will be collected and analyzed offsite using the EPA SW-846 method semiannually to confirm the onsite data.

5.2.2 Ethene/Ethane/Methane

These compounds will be analyzed at the IRC using a GC equipped with a flame ionization detector (FID). see ISB FEWP SAP (Sorenson and Bullock 1999). Again, these samples will also be analyzed at an offsite laboratory semiannually to confirm the onsite data.

5.2.3 Electron Donor/Lactate

Samples collected for electron donor analysis will be analyzed at the IRC. Lactate concentration will be determined in a filtered sample using a Dionex 4000I ion chromatograph with a conductivity detector. Again, please reference the ISB FEWP SAP (Sorenson and Bullock 1999) for a more complete analytical description.

5.2.4 Acetate/Propionate/Butyrate

The acetate, propionate, and butyrate analysis will be conducted at the IRC. Concentrations of acetate, propionate, and butyrate will be analyzed by diluting the filtered sample with an equal volume of pH 2.5 deionized water and then directly injecting 1 μ L into a HP Model 5890 Series II GC equipped with a FID, as described in the ISB FEWP SAP (Sorenson and Bullock 1999).

5.2.5 Tritium

Groundwater samples collected for tritium will be analyzed at an offsite laboratory following the guidelines specified in Environmental Restoration Scope of Work (ER SOW)-163. The required detection limit will be as specified in Table 4-1 of ER-SOW-163.

5.2.6 Beta-and Gamma Emitters

Groundwater samples will be collected quarterly for the analysis of Cs-137 and Sr-90. These samples will be analyzed at an offsite laboratory following the guidelines set forth in ER-SOW-163.

5.2.7 Alpha Emitters

Groundwater samples will be collected annually for the analysis of alpha emitters. These samples will also be analyzed at an offsite laboratory following the guidelines set forth in ER-SOW-163.

5.2.8 Metals

Groundwater samples will be collected annually for the analysis of metals using the Contract Laboratory Program target analyte list per the appropriate SW-846 method.

5.2.9 Field Analyses

Refer to Table 5-3 for the analytical parameters and associated methods to be used for field analyses.

6. WASTE MANAGEMENT

Listed waste will be generated at Operable Unit 1-07B as a result of sampling activities discussed herein. The types, disposition, and handling of listed waste that will be generated are discussed below.

The sampling activities described above will generate potentially contaminated wipes, sample bottles, personal protective equipment (i.e., gloves), sample rinseate, and purge water. All of the solid materials will be bagged and labeled with the contents, waste code F001 for TCE, and mixed waste. The waste will be transferred to the storage area for storage with Waste Stream 1935 under direction of the operations supervisor. Unaltered sample rinseate and purge water will be taken to the ASTU located at well TAN-29 where it will be treated and discharged to well TAN-49. The ASTU will continue to be operated intermittently for the purpose of purge water and sample treatment. Concentrations of TCE in all water treated by the air stripper will be reduced below the maximum contaminant level of 5 µg/L before reinjection, to meet the no-longer-contained-in requirements defined by the IDEQ Hazardous Waste Permitting Bureau (IDeq, 1998). Sample residue from field analysis will be disposed and managed per the hazardous waste determination for the Operable Unit 1-07B TAN Groundwater Remediation Field Lab Residuals Bioremediation Treatability Study, Revision 1.

Waste management of sample residues generated from offsite and research samples will be the responsibility of the laboratory and/or organization for which the samples were collected. The waste will always carry the F001 waste code, and may also be mixed waste. The chain of custody form will specify the appropriate classifications for the sample residues.

7. QUALITY ASSURANCE

This plan is intended to be used in conjunction with the QAPjP and *Implementing Project Management Plan for the Idaho National Engineering and Environmental Laboratory Remediation Program*, INEEL/EXT-97-00032, Section 13, Quality Assurance. The data quality indicators will be as specified in the QAPjP for all samples sent offsite for analysis. Required precision and accuracy for all analytical methods were given in Tables 2-2, 2-3, and 2-4. Duplicates, field blanks, trip blanks, and rinseates will be used as specified in the QAPjP for all samples sent offsite (Table 7-1). The completeness goal for all samples will be 90%. The performance monitoring and secondary source mobilization samples are considered noncritical. All of the data to be collected during the predesign operations period will be used to evaluate relatively long-term changes in analytes; thus, no single sample is critical to the interpretation.

The quality level determined for all sampling activities in this plan is quality Level 3 in accordance with the project management plan and MCP-540, "Graded Approach & Quality Level Assignment." While the analytical data category required for this application is that of screening data per *Data Quality Objectives Process for Superfund* (EPA 1994) and the QAPjP, most of the quality assurance/quality control elements for definitive data will be used. Definitive confirmation will be provided for the chloroethene data and the ethene/ethane/methane data by sending splits to an offsite laboratory semiannually (Table 7-2). The definitive data will undergo level A validation. All other data are being analyzed at onsite laboratories and will undergo level X validation.

For the analysis of water quality parameters in the field, the manufacturer's instructions will be used to ensure accuracy. At least 5% of the samples will include replicate analysis (one in twenty samples analyzed twice) and 5% of the samples will be duplicates to estimate the analytical precision and the total measurement error, respectively. Check standards will be used as necessary to ensure the accuracy of each field analysis (see TPR-166). The primary concern for groundwater elevation measurements is the effect of barometric fluctuations. In order to provide data to help account for this effect, a barometric transducer will be placed in one of the wells. The pressure transducer performance will also be checked by manually measuring the depth to water.

Table 7-1. Quality assurance/quality control samples for groundwater analyses.

Activity	Type	Comments
Groundwater Analyses	Duplicate	Field duplicates will be collected at a frequency of 1 per 20 samples
	Field Blank	Field blanks will be collected at a frequency of 1 per sampling event for radiological analyses only
	Trip Blank	Trip blanks will be collected 1 per sampling event for VOCs and ethene/ethane/methane analyses only
	Split	Splits will be taken semiannually for chloroethenes and ethene/ethane/methane.

Table 7-2. Specific requirements for groundwater split samples.

Analytical Parameter	Size	Type	Preservative	Method	Holding Time
Chloroethenes	40-mL	Two Glass Vials	pH to <2 w/H ₂ SO ₄ , 4°C	SW-846 8260B	14 days
Ethene/Ethane/ Methane	40-mL	Two Glass Vials	pH to <2 w/H ₂ SO ₄ , 4°C	SW-846 8015M/3810M	14 days

7.1 Laboratory Performance Evaluation

In addition to routine internal laboratory quality control protocol, the IRC laboratory analyzing water samples for chloroethenes will participate in a monthly performance evaluation (PE) program. The offsite laboratory confirming the onsite data will receive PE samples semiannually. The PE program is administered through the INEEL SMO using commercially supplied and certified standards obtained from an independent supplier. The IRC laboratory will receive two water PE samples per month for analysis. The offsite laboratory will receive double blind PE samples with the shipment of field samples to be analyzed. The double blind PE samples will be prepared and obtained from the independent supplier and shipped to the field crew to be included with the appropriate field samples. The IRC will also receive double blind PE samples for the semiannual split round.

The PE sample type (blank, low-level, etc.) is distributed randomly with varying concentrations of target analytes and at the established frequency shown in Table 7-3. At the direction of the SMO program administrator, one of the two monthly samples will be analyzed in duplicate to obtain precision information. The monthly water PE samples are shipped directly from the supplier as sealed ampoules and will be prepared at the laboratory by the analyst according to the dilution instructions accompanying each shipment. The supplier provides the certified values and round robin data (analysis results generated by laboratories independent of the supplier) to the SMO program administrator under separate cover to ensure confidentiality.

The laboratory analyst will provide their PE analytical results to the SMO program administrator for comparison to the certified values. Any deviations from the preparation instructions (such as additional dilutions to meet instrument calibration range) must be noted and provided with the final results sent to the SMO program administrator.

Table 7-3. Summary of performance evaluation program for water samples.

Type of PE Sample	Concentration Range	Frequency of PE Sample Type Per Year	Target Analytes Evaluated
Blank	0 µg/L	3	trichloroethene tetrachloroethene trans-1,2-dichloroethene cis-1,2-dichloroethene 1,2-dichloropropane vinyl chloride
Low-level	5 to 10 µg/L	9	trichloroethene tetrachloroethene trans-1,2-dichloroethene cis-1,2-dichloroethene 1,2-dichloropropane vinyl chloride
Mid-level	5 to 100 µg/L	9	trichloroethene tetrachloroethene trans-1,2-dichloroethene cis-1,2-dichloroethene 1,2-dichloropropane vinyl chloride

As shown in Table 7-4, acceptance criteria for analytical accuracy are defined for each target analyte using the round robin data (if available) provided by the supplier. Warning limits are defined as the concentration range ± 2 standard deviations around the mean concentration from the round robin study. Action limits are defined as the range ± 3 standard deviations around the mean concentration. If round robin data are not available (i.e., blanks), the warning and action limits are based on the SW-846 Method 8260A guidelines for percent recovery and the estimated quantitation limit for a 25 mL purge volume (1 µg/L). The acceptance criterion for analytical precision, expressed as relative percent difference, is 20%.

Table 7-4. Acceptance criteria for analytical accuracy in water performance evaluation analyses.

Limits	Round Robin Data Available	Round Robin Data Unavailable	Blanks
Warning limits	Mean concentration ± 2 standard deviations	Certified value $\pm 25\%$	$<1 \mu\text{g/L}$
Action limits	Mean concentration ± 3 standard deviations	Certified value $\pm 30\%$	$<1.5 \mu\text{g/L}$

Corrective action is recommended when results fall outside the corresponding warning limits and within the action limits. Corrective action is required when results fall outside the corresponding action limits. Corrective action is also required when results fall outside the corresponding warning limits with the same analytical trend (i.e., low bias or high bias) for three consecutive evaluation periods.

Specific corrective actions are left to the discretion of the analyst. The effectiveness of the performed corrective actions will be evaluated by performing a verification analysis. A standard that is a second source to the calibration standards will be analyzed, and the recovery of the target analytes will meet the accuracy criteria for the corresponding warning limits. If the laboratory chooses, the PE sample may be used as the verification standard provided that the verification analysis is completed within 14 days from the original date of sample preparation. The laboratory analyst will provide the SMO program administrator a brief, written description of the corrective action performed and the verification data to substantiate the adequacy of that corrective action.

8. REFERENCES

- DOE-ID 1995, *Record of Decision: Declaration for the Technical Support Facility Injection Well (TSF-05) and Surrounding Groundwater Contamination (TSF-23) and Miscellaneous No Action Sites Final Remedial Action, Operable Unit 1-07B, Waste Area Group 1*, Idaho National Engineering Laboratory, Idaho Falls, Idaho.
- DOE-ID 1997, *Quality Assurance Project Plan for Waste Area Groups 1, 2, 3, 4, 5, 6, 7, 10 and Inactive Sites*, DOE/ID-10587, Revision 5.
- DOE-ID 1998, *Enhanced In Situ Bioremediation Field Evaluation Work Plan, Test Area North, Operable Unit 1-07B*, DOE/ID- 10639, Revision 0.
- DOE-ID 2000, *Field Demonstration Report, Test Area North Final Groundwater Remediation, Operable Unit 1-07B*, DOE/ID-10718, Revision 0.
- EPA 1990, *National Oil and Hazardous Substances Contingency Plan*, Federal Register, Volume 55.
- EPA 1994, *Data Quality Objectives Process for Superfund, Interim Final Guidance*, EPA 540-R-93-071.
- IDEQ, 1998, Letter from Hazardous Waste Permitting Bureau Chief B.R. Monson to LMITCO Deputy Director of Environmental Affairs C.R. Koshuta, September 17, 1998.
- INEEL 1998, *Health and Safety Plan for Test Area North Final Groundwater Remedial Action Operable Unit 1-07B*, INEEL/EXT-98-00403, Revision 0.
- Kaminski, J. F., K. N. Keck, A. L. Schafer-Perini, C. F. Hersley, R. P. Smith, G. J. Stormberg, and A. H. Wylie, 1994, *Remedial Investigation Final Report with Addenda for the Test Area North Groundwater Operable Unit 1-07B at the Idaho National Engineering Laboratory*, EGG-ER-10643.
- Sorenson, K.S. and H. Bullock, 1999, *Sampling and Analysis Plan for the Enhanced In Situ Bioremediation Field Evaluation Test Area North, Operable Unit 1-07B*, INEEL/EXT-98-00421, Revision 1.

Appendix A
Agency Comment Responses

PROJECT DOCUMENT REVIEW RECORD

Document Title/Description: Sampling and Analysis Plan for Enhanced In Situ Bioremediation Predesign Operations Test Area North, Operating Unit 1-07B

Date: September 11, 2000 Reviewer: Mark Jeffers, State of Idaho, Department of Health and Welfare, Division of Environmental Quality;
EPA Public Communications Office

ITEM NUMBER	SECTION NUMBER	PAGE NUMBER	COMMENT	RESOLUTION
1	Section 2.4.2		Considering the current high concentrations of lead and other metal constituents, an annual sampling and analysis for metals is inadequate. Until an explanation for these elevated concentrations is established and concentration trends are downward, more frequent monitoring for metals is necessary.	Comment incorporated. The sampling and analysis interval for total metals will be revised to quarterly, from the current bimonthly schedule, beginning November 2000.
2	Section 4.2		Data should be presented to support a comparative analysis of analytical results for micro purging vs. standard purging results for wells which may have been previously sampled using the standard three well bore volume methodology. If adequate data does not exist, comparative analytical data must be obtained prior to DEQ's acceptance of this purge method.	Comment incorporated. As discussed in agency conference calls, this report will be prepared in FY 2002.
3	Section 6 6 th Sentence		The statement that reinjected water for these wells with TCE concentrations below 5Φg/L, will no longer contain F001 – listed waste is not accurate. To make this statement true, a no-longer-contained-in determination must be granted by the State of Idaho.	Comment incorporated. The 9/17/98 letter from the IDEQ Hazardous Waste Permitting Bureau Chief granting NLCI status to ASTU effluent treated to less than 5 μg/L TCE will be cited as the basis for the NLCI determination.